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One-Pot Synthesis of *N*-Unprotected Azacyclopentylidene Complexes from their Oxa Analogues[1]

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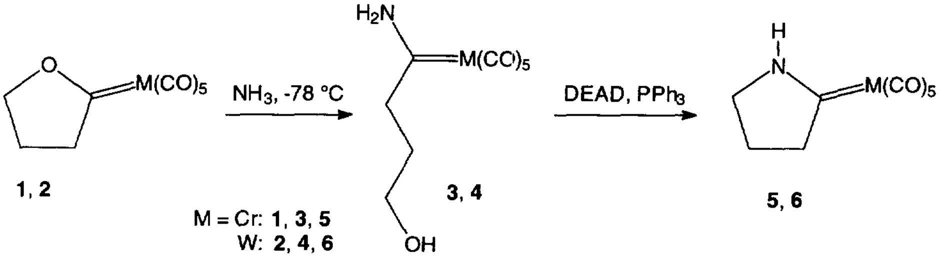
Abstract

N-Unprotected azacyclopentylidene complexes of chromium and tungsten have been prepared from their oxacyclopentylidene analogues in a tandem aminolysis/Mitsunobu recyclization reaction.

Keywords: Carbene complexes; Cyclization; Mitsunobu reaction

Fischer aminocarbene complexes have found increasing application in stereoselective organic synthesis [2]. The α-CH-acidity of cycloalkylidene complexes has been exploited in an *exo*-alkenylation followed by spiro-cycloaddition and annelation reactions. While oxacyclopentylidene complexes are easily accessible via cyclization of alkynols at the metal template [3], no general access to their azacyclopentylidene congeners is available to-date [4].

We report here on an efficient and simple one-pot procedure for the conversion of oxacyclopentylidene complexes of chromium and tungsten into their *N*-unprotected azacyclopentylidene analogues based on a tandem ring-opening ammonolysis [5] and Mitsunobu recyclization [6] sequence as recently developed for the preparation of chromium iminofuranosylidene complexes [7].



Scheme 1: One-pot preparation of azacyclopentylidene complexes.

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Gaseous ammonia was condensed into dilute solutions (30-40 mM; **1**: CH_2Cl_2; **2**: Et_2O) of oxacyclopentylidene complex which immediately and quantitatively generated acyclic aminocarbene complexes **3** and **4**. The solvent was changed for THF (30-40 mM), 1.5 eq of triphenylphosphine (PPh_3) and 1.3 eq diethyl azodicarboxylate (DEAD) were added, and the solution was stirred overnight. The azacyclopentylidene complexes were purified by column chromatography on silica gel (**5**: light petroleum/Et_2O/acetic acid 7:1:1; **6**: light petroleum/Et_2O 3:1), yielding **5** (65 %) and **6** (88 %) as yellowish powders [8].

Acknowledgement

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[8] Selected spectroscopic data for **4**: IR (light petroleum): 2062, 1965, 1929 cm^{-1}. ^1H NMR (400.13 MHz, C_6D_6) 1.20 (tt, 7.1 Hz, 5.8 Hz, 2 H), 2.45 (t, 7.1 Hz, 2 H), 2.92 (t, 5.8 Hz, 2 H), 7.22, 7.95 (br, 2 H). ^{13}C NMR (125.76 MHz, C_6D_6): 28.9, 53.1, 60.8 (3 C), 198.8 (4 C, CO_{cis}), 202.9 (1 C, CO_{trans}), 266.9 (1C, C-1). HRMS: $C_9H_9NO_6W$ calc.: 408.9913, found: 408.9916. For **5**: IR (light petroleum): 2054, 1965, 1927 cm^{-1}. ^1H NMR (500.13 MHz, C_6D_6): 0.77 (quint*, 7.8 Hz, 2 H), 2.25 (t, 7.8 Hz, 2 H), 2.55 (t, 7.7 Hz, 2 H), 7.08 (br, 1 H). ^{13}C NMR (100.61 MHz): 20.0, 53.2, 54.7 (3 C), 218.4 (4 C, CO_{cis}), 223.4 (1 C, CO_{trans}), 271.2 (1 C, C-1). HRMS: $C_9H_7NO_5Cr$ calc.: 260.9730 found: 260.9733. $C_9H_7NO_5Cr$ (262.16) calc.: C 41.39, H 2.70, N 5.36; found: C 41.48, H 2.82, N 5.13. For **6**: IR (light petroleum): 2062, 1925 cm^{-1}. ^1H NMR (400.13 MHz, C_6D_6): 0.78 (quint*, 7.83 Hz, 2 H), 2.19 (tq, 7.83 Hz, 1.17 Hz, 2 H), 2.41 (tq, 7.83 Hz, 1.87 Hz, 2 H), 6.90 (br, 1 H). ^{13}C NMR (100.62 MHz, C_6D_6): 21.0, 55.4, 55.8 (3 C), 199.3 (4 C, CO_{cis}), 204.1 (1 C, CO_{trans}), 249.9 (1 C, C-1). HRMS: $C_9H_7NO_5W$ calc.: 390.9806, found 390.9801.